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GROWTH OF ZnS:Ag:Cu THIN FILM DEPOSITED ON GLASS SUBSTRATES USING THERMAL EVAPORATION TECHNIQUE FOR ALPHA-PHOTOVOLTAIC

Emy Mulyani[1], Tjipto Sujitno[1], Dessy Purbandari[2], Ferdiansjah[2] and Sayono[1]
Centre for Accelerator Science and Technology - National Nuclear Energy Agency
Jl. Babarsari Kotak Pos 6101, Yogyakarta, Indonesia
[2]Department of Nuclear Engineering, Faculty of Engineering - Gadjah Mada University
Bulaksumur, Yogyakarta 55281
E-mail: emymulya@batan.go.id

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ABSTRACT

GROWTH OF ZnS:Ag:Cu THIN FILM DEPOSITED ON GLASS SUBSTRATES USING THERMAL EVAPORATION TECHNIQUE FOR ALPHA-PHOTOVOLTAIC. This paper presents the research on the growth of ZnS:Ag:Cu thin film on a glass substrate as a radio-luminescent material. The SRIM/TRIM software is used to determine the optimum thickness based on an energy deposition depth of 5.485 MeV Am 241 alpha radiation source on ZnS:Ag:Cu material. To increase the adhesive strength of the coating, initially, the glass substrate is etched using a plasma glow discharged at 280°C for 15 minutes. Multiple coatings of ZnS:Ag:Cu were deposited on the glass substrate; this was carried out using a thermal evaporation technique to achieve the optimal thickness (based on SRIM/TRIM simulation). The thin film thickness was observed using a scanning electron microscope (SEM). The optical properties of the un-etched substrate, etched substrate and thin-film samples were characterized using UV-Vis spectrometer. Based on SRIM/TRIM simulation, the optimal thickness is 22 mm which can be achieved by coating three times. From optical properties of ZnS:Ag:Cu thin film and after being analysed using Tauc's plot method, it is found that the energy gap of ZnS:Ag:Cu thin film is 2.48 eV.

Keywords: Plasma nitridation, ZnS:Ag:Cu thin layer, Thermal evaporation, Glass substrate, Deposition

ABSTRAK

PERTUMBUHAN LAPISAN TIPIS ZnS:Ag:Cu UNTUK ALPHA-PHOTOVOLTAIC YANG DIDEPOSISIKAN PADA SUBSTRAT KACA MENGGUNAKAN TEKNIK EVAPORASI TERMAL. Makalah ini menyajikan penelitian terkait pertumbuhan lapisan tipis ZnS:Ag:Cu pada substrat kaca sebagai [illegible] optimal [illegible] S:Ag:Cu. Untuk meningkatkan kekuatan rekat lapisan, substrat kaca di etsa pada plasma 280° C selama 15 menit. ZnS:Ag:Cu dideposisikan pada substrat kaca menggunakan teknik penguapan termal untuk mencapai ketebalan optimal (berdasarkan simulasi SRIM/TRIM). Berdasarkan simulasi SRIM/TRIM, ketebalan optimal adalah 22 mm yang dapat dicapai dengan pelapisan tiga kali. Ketebalan lapisan tipis diamati menggunakan scanning electron microscope (SEM). Sifat-sifat optik dari substrat (dengan etsa dan tanpa etsa) dan lapisan tipis dikarakterisasi menggunakan spektrometer UV-Vis. Dari sifat optik ZnS:Ag:Cu setelah dianalisis menggunakan metode plot Tauc, ditemukan bahwa energi gap lapisan tipis ZnS: Ag:Cu adalah 2,48 eV.

Kata kunci: Nitridasi plasma, Lapisan tipis ZnS:Ag:Cu, Evaporasi termal, Substrat kaca, Deposisi

INTRODUCTION

Zinc sulphide (ZnS) is an abundant and environmentally friendly semiconductor material. The ZnS material has a wide energy band gap of around 3.66 eV, good chemical stability, large light transmittance, and small scattering in areas of visible and infrared light [1]. Because of its properties, this material can be used in numerous applications e.g. solar cells [2, 3], optoelectronic devices [4], photocatalyst [5], and photovoltaic [6]. ZnS also has the potential to be used as a radiation material on alpha-photovoltaic type nuclear battery applications [7-11]. Unfortunately, the energy gap of ZnS is quite high (3.6 eV) [6], [12-15]. Doping is one strategy for reducing the bandgap, thus increasing visible light absorption [16]. There are several techniques available to prepare the ZnS thin films such as thermal evaporation [17,18], chemical bath deposition [19-21], electron beam evaporation technique [22], spray pyrolysis [23,24], sputtering technique [25], and Successive on Layer Adsorption and Reaction (SILAR) technique [26].

Nuclear batteries have potential to be substitutes for conventional battery because they have an energy density 1000 times greater than chemical batteries, long operating time, and good resistance to extreme environmental conditions [26]. The power scale of nuclear batteries is from μW up to mW which can potentially supply power to sensors and low-power electronic devices. One of the uses of low power sensors and electronics is as a marker of the location of stakes at the border. To supply electronic devices at the border, a continuous supply of power, long operating time, small size, and good resistance to extreme environmental conditions is needed. For that reason, the development of nuclear batteries as an alternative resource is suggested.

The radio-luminescent layer converts radiation from radioactive sources into photons which are then converted to electricity (photovoltaic effect). The performance of the photovoltaic device is influenced by several factors such as the characteristics of the radio-luminescent layer and substrate transmittance. The characteristics of the radioluminescence layer include coating thickness and material bandgap. The design needs to be the right thickness so that it can absorb radiation optimally. Characterization of the radio-luminescent layer band gap values is needed to determine the required photovoltaic specifications.

Determination of the optimal thickness based on energy deposition depth is simulated using the SRIM/TRIM program. The SRIM (The Stopping and Range of Ions in Matter) is a group of programs which calculate the stopping and range of ions into matter using a quantum mechanical treatment of ion-atom meanwhile, TRIM (the Transport of Ions in Matter) will calculate both the final 3D distribution of the ions and also all kinetic phenomena associated with the ion's energy loss: target damage, sputtering, ionization, and phonon production. The depth of radiation through the material is determined by the type of radiation, radiation energy, and type of material [1]. The theoretical values obtained are then used as a reference for the thick coating of radio-luminescent material. The aim of this research is to study the effect of Ag and Cu dopant on the energy gap and optical properties of ZnS thin films deposited on glass substrate using a thermal evaporation technique. This technique was chosen because the results are distributed more homogeneously, it is relatively easy to apply, and it does not require a mixture of hazardous chemicals. However, sometimes the material deposited using this technique cannot attach firmly to the surface of the substrate. To overcome this problem, plasma etching techniques were carried out on the surface of the glass substrate. The purpose of this treatment is to make the glass surface rough so that the radio-luminescent material will attach firmly on the glass surface.

EXPERIMENTAL METHOD

Commercially glass substrates were cleaned before deposition in the ultrasonic bath using methanol-acetone-methanol, deionized water sequence for 15 minutes each followed by the drying with industrial nitrogen gas. Then the glasses were etched using plasma argon (Ar) for 8, 10, and 15 minutes at 250°C and 280°C. Then the sample was removed from the plasma reactor tube. Next, the sample was attached in the substrate holder of the evaporation chamber. A boat with the distance of 11 cm from the substrate was maintained throughout the experiment. In our evaporation machine, 11 cm is the optimum distance for evaporation. ZnS:Ag:Cu powder was deposited on the etched glass substrates using high purity ZnS:Ag:Cu (United Nuclear, 1% Ag and 1% Cu). Vacuum condition was attained inside the thermal evaporation chamber with the combination of rotary and diffusion pumps. After reaching a vacuum level of 10^{-6} torr, the DC across the boat was gradually raised to heat ZnS:Ag:Cu powders to temperatures greater than the melting point. This allowed the evaporation of ZnS:Ag:Cu material. Each coating needs 0.3185 grams of ZnS:Ag:Cu powder and a distance between the glass substrate and the boat of 11 cm. After coating, the thickness of the coating was observed using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Etching of Glass Substrate

The main purpose of the etching process is to increase the adhesion of the coating even though the transmittance will decrease. Effect of etching at 250°C and 280°C for 8, 10, and 15 minutes are presented in Figure 1.

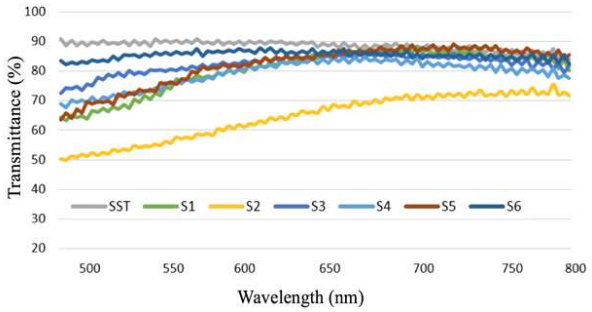

Figure 1. Effect of etching time on the transmittance of glass substrate.

Figure 1 shows that the effect of dry etching will reduce the transmittance of the glass substrate. SST is non-etching, S1 is etching at 250°C for 8 minutes, S2 is etching at 250°C for 10 minutes, S3 is etching at 250°C for 15 minutes, S4 is etching at 280°C for 8 minutes, S5 is etching at 280°C for 10 minutes, and S6 is etching at 280°C for 15 minutes. This phenomenon can be explained as bombardments of energetic ion beams then form textures on the surface of the glass. The effect of the texture causes the light to not be directly transmitted or reflected when it hits the surface, some of the light will be reflected out, some of it will be forwarded. From Figure 1, it can be concluded that etching at 280°C for 15 minutes produced the best transmittance value at 450 nm to 650 nm.

Deposition of ZnS:Ag:Cu

The coating process was carried out on four glass samples with different thicknesses of coatings. Four samples were coated with a distance of 11 cm from the substrate to the boat and a mass for each coating of 0.3187 gram. If the current flowing into the boat is too high, then ZnS:Ag:Cu powder will easily scatter so that only a little of ZnS:Ag:Cu is evaporated to the substrate. Thus, the current flowing must be set from 120 up to 125 A. Each layer usually has around ~ 0.03 grams which do not evaporate. To avoid excessive heating of the glass substrate, the temperature was set to 450°C for 20 minutes. If the coating time is too long, it causes ZnS:Ag:Cu material loosely attached to the glass surface. As a result, many layers formed and then peeled off when the glass is removed from the vacuum vessel. The condition of the peeling layer gets worse when the glass is left idle for several days even though it is stored in a closed container. To avoid this, it is necessary to set the coating time, the total current flowing to the boat, the distance of the substrate and target, and vacuum in the vessel to produce the best conditions. Figure 2 shows the cross-section morphology of ZnS:Ag:Cu thin film deposited at one, two, three ,and seven times coatings.

Figure 2 shows the results of coating four samples with different amounts of coating treatment. Figure 2 (a)

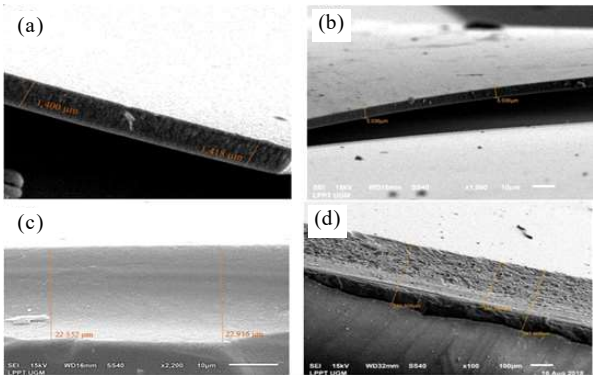

Figure 2. Cross-section morphology of ZnS:Ag:Cu thin film deposited at (a). one-time coating, (b). two times coating, (c). three times coating, and (d). seven times coating.

shows the cross-section of the ZnS: Ag: Cu layer sample, which was coated once with a thickness of 1.418 μm; 1.203 μm; 1.400 μm. Figure 2 (b) shows the cross-section of the ZnS: Ag: Cu layer sample, which was coated twice with a layer thickness of 5.036 μm. Figure 2 (c) shows the cross-section of the ZnS: Ag: Cu layer sample which was coated three times with a layer thickness of 22.552 μm; 22.916 μm. Figure 2 (d) shows the cross-section of the ZnS: Ag: Cu layer sample, which was coated seven times with a layer thickness of 333.808 μm; 347.908 μm. From the cross-section of the ZnS: Ag: Cu layer above, it can be seen that the addition of the coated mass increases the thickness of the layer produced by varying thickness increases. SRIM / TRIM simulation showed that 5.485 MeV alpha energy will stop at a depth of about 21-22 μm when passing through ZnS:Ag:Cu material. So, to get the optimal thickness, the coating is carried out three times. Each coating needed to be 0.3187 grams of ZnS:Ag:Cu material, and the distance of the boat to the glass substrate was 11 cm. Figure 3 shows the surface morphology of the thin layer formed from the evaporation of ZnS: Ag: Cu. Powder. Figure 4 shows the absorbance of the ZnS:Ag:Cu layer as a function of the visible light wavelength.

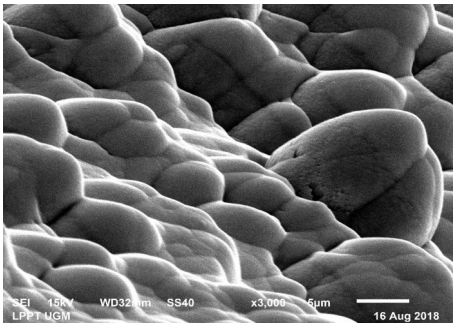

Figure 3. Surface morphology of ZnS:Ag:Cu thin film deposited at three times coating (22.552 μm of thickness layer).

Based on Figure 4, it can be seen that the absorption peak occurs at wavelengths of 410 nm to

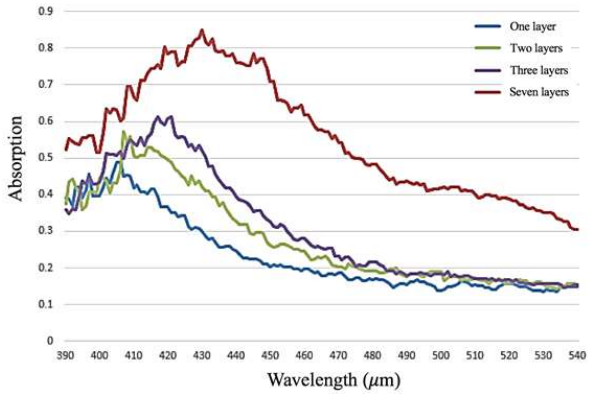

Figure 4. The absorbance of the ZnS:Ag:Cu layer as a function of the visible light wavelength.

460 nm. This is under the theory that ZnS emits the most photons in the blue energy spectrum and will shift to the green energy spectrum when transition metal impurities were added [1]. (From Figure 4 it can be seen, for a thicker layer, there is a shift in the absorption peak of the ZnS: Ag: Cu layer. That the formed absorption peak increasingly shifts right for thicker samples, indicates that the photon energy spectrum is getting closer to the green spectrum. Samples which are coated once have absorption peaks at wavelengths of 405 to 406 nm. The sample coated two times has an absorption peak at a wavelength of 407 nm. The sample coated three times has two absorption peaks namely at wavelengths of 417 nm and 421 nm. Finally, samples coated seven times have absorption peaks at a wavelength of 530 nm. Figure 4 also showed that the samples for one coating, two coatings, and three coatings have lower absorbance values than samples coated seven times. This is because the seven-time coating sample has a coating thickness greater than the other samples so it absorbs more light. The relationship between material thickness and absorbance is directly proportional, or inversely proportional to transmittance.

The value of absorbance data from UV-Vis spectroscopic tests was analyzed using the Tauc Plot method; the result is presented in Figure 5. The x-axis is photon energy (eV) which is calculated for each

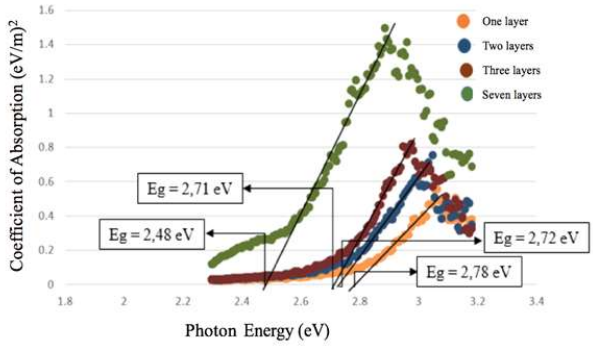

Figure 5. The relationship between the absorbance coefficient and the photon energy in the ZnS:Ag:Cu layer.

wavelength of visible light. The y-axis is multiplication squared of the coefficient of absorbance with the square of the photon energy. The linear data in the graph is then extrapolated to cut the x-axis. From extrapolation, the bandgap value of ZnS: Ag: Cu is obtained at 2.48 eV. According to the theory, the bandgap of ZnS is 3.6 eV. After being doped with 1% Ag and 1% Cu (based on the material data sheet from United Nuclear), the bandgap is reduced to 2.48 eV. This value is very appropriate for photovoltaic devices to convert visible light from the ZnS: Ag: Cu layer to electricity. In addition, the doped film has the highest absoption efficiency for visible light in the blue-green spectrum.

CONCLUSION

Based on SRIM / TRIM simulation, an optimal thickness of ZnS:Ag:Cu thin film which can absorb alpha energy of 5.485 MeV is 22 μm. Experimentally, this thickness was achieved after coating three times with each coating needing 0.3187 grams of ZnS:Ag:Cu powder. Plasma etching treatment affects the value of transmittance of glass samples. The etched glass substrate has lower transmittance values than the non-etched glass substrate. The best transmittance at wavelengths of 450 nm to 650 nm was achieved at 280ºC and 15 minutes of etching time. Based on the results of the characterization of optical properties using UV-Vis spectroscopy and after being analyzed using the Tauc Plot method, it was determined that the bandgap of ZnS:Ag:Cu thin layer is 2.48 eV.

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